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The dimpling in the CuO_2 planes of $YBa_2Cu_3O_x$ (x=6.806-6.984, T=20-300 K) measured by yttrium EXAFS

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Abstract

The dimpling of the CuO_2 planes (spacing between the O2,3 and Cu2 layers) in $YBa_2Cu_3O_x$ has been measured as a function of oxygen concentration and temperature by yttrium x-ray extended-fine-structure spectroscopy (EXAFS). The relative variations of the dimpling with doping ($x = 6.806 - 6.984$) and temperature (20-300 K) are weak (within 0.05 Å), and arise mainly from displacements of the Cu2 atoms off the O2,3 plane towards Ba. The dimpling appears to be connected with the transition from the underdoped to the overdoped regimes at $x = 6.95$, and with a characteristic temperature in the normal state, $T^* \simeq 150$ K.

1 Introduction

Coherent structural distortions of the superconducting CuO_2 planes appear to be a crucial issue of the high-T_c cuprates [1]. The dimpled basal planes of the CuO_5 pyramides in $YBa_2Cu_3O_x$ emerged already from early crystallographic work on this material. Tilts of the CuO_6 octahedra in the La 214 family are frequently considered to be at the origin of mesoscopic stripe patterns found in some of their compounds. And, as it is well known, the Bi family of superconductors exhibits long range order modulations of the CuO_2 layers. On the other side, the superconducting Hg cuprates (exhibiting the highest T_c's) were found to have undistorted CuO_2 planes. But recent crystallographic work seems to converge to relatively weak dimples ($\simeq 0.05$ Å) in the basal planes of the CuO_5 pyramides of the two and more layer Hg compounds [2].

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The displacements leading to an effective transversal modulation of the CuO_2 planes may be of different kind and physical origin. "Buckling" in the La 214 family and the long range order modulations in the Bi family are understood to arise from tilts of the CuO_6 octahedra and the CuO_5 pyramides, respectively, both exhibiting *flat* basal planes. On the other hand, the displacements of the planar Cu and/or planar O atoms along c labeled "dimples" imply the basal O–Cu–O bonds to be no longer rigid but soft, and to be bent in c direction. The dimpling in metallic Y-123 is ≥ 0.25 Å [3,4], but ≤ 0.05 Å in metallic Hg-1212 [2]. We conclude that also other physical properties than metallicity and superconductivity may be at the origin of the dimpling, and the net effect possibly attributable to the superconductivity in the high-T_c cuprates may be as small as 0.05 Å. Important consequences from this conclusion arise for both, experimental and theoretical work.

First, the structural distortions possibly relevant for the superconductivity in doped Mott insulators depend on the carrier concentration. Since the doped charge carriers are not expected to be randomly distributed in the CuO_2 planes, the resulting structural deformations most likely break the translational invariance of the underlying lattice. Local probes are therefore important experimental tools for the investigation of this structural problem.

Second, if the dimpling of the CuO_2 planes is connected to the mechanism of superconductivity in the cuprates, it is not justified to consider their copper oxygen chemistry in the usual way as forming rigid, strong bonds between the copper atom and the four oxygens. Consequently theoretical work has to allow for dynamical degrees of freedom to treat the oxygen and copper orbitals separately. The theoretical understanding of the experimentally apparent "soft" or bent Cu–O bonds is still at its infancy. But a recent study of the correlations in a high-T_c cuprate using the Local Ansatz showed that the charge transfer inside the Cu atoms is much larger than that between the planar Cu and O atoms, due to correlations [5]. This finding stresses the need for that atomic correlations of the copper orbitals $(3d - 4s, p)$ have to be taken into account to understand the "soft" Cu–O bonding in doped cuprates.

In this brief report we are presenting measurements of the dimpling in the CuO_2 planes of $YBa_2Cu_3O_x$ by yttrium EXAFS, as a function of temperature and doping on both sides of the underdoped-overdoped phase separation line at $x = 6.95$.

2 Experimental Details

The photoexcited cations in the separating sheet of the two layer cuprates are ideal observers of the local atomic structure of the CuO_2 planes. We have

measured the EXAFS beyond the yttrium K edge up to $k \simeq 20$ Å^{-1} from fine grains ($\leq 5\mu$m) of $YBa_2Cu_3O_x$ ($x = 6.806 - 6.984$) synthezised under near equilibrium conditons. Details of the x-ray spectroscopy, the data reduction, and of the synthesis of the samples are given elsewhere [6].

The positions and the vibrational dynamics of the O2,3 and Cu2 atoms can be extracted from the nearest and next nearest neighbour two-body scattering configurations Y–O2,3; Y–Cu2, and the nearly collinear three-body multiple scattering (MS) configurations Y–O2,3–Ba ($\simeq 5$ Å), Y–Cu2–Ba ($\simeq 6.2$ Å). To determine the dimpling as a function of temperature we have exploited the high sensitivity of these two MS configurations to static displacements of the intervening O2,3 and Cu2 atoms, respectively. Since both MS configurations include the same Ba-layer, the ratio of their experimental scattering amplitudes cancels to first order approximation the effects arising from thermal disorder, and the temperature dependent variations of the Y–Ba distances. Thus we are able to separate the desired information on the static positional changes from the thermal disorder, thereby avoiding weakly based assumptions on the vibrational dynamics of the Y–Ba cluster.

3 Experimental Results

Fig.1 exhibits the temperature and concentration dependencies of the effective scattering amplitudes of Y–O2,3–Ba (open circles) and Y–Cu2–Ba (closed circles) for three underdoped ($x = 6.806 - 6.886$) and two overdoped samples ($x = 6.968, 6.984$); $x = 6.947$ is close to optimum doping ($x = 6.92$). The average temperature dependencies exhibit significant deviations from the $1/coth(1/T)$ behaviour expected from harmonic motions of the diatomic pairs Y–Ba. In addition dips and step-like features occur in the normal conducting temperature region. $x = 6.886$ exhibits a clear jump at 110 K. We have carefully checked the sources of systematic errors possibly giving rise to the discontinuities in the effective scattering amplitudes, in particular the normalization of the experimental absorption coefficient. As a result we can definitely exclude experimental artefacts to be at the origin of the dips in $x = 6.806$, $x = 6.947$, and of the step in $x = 6.886$ around 120 K. We note that the experimental spectra of $x = 6.886$ exhibit the relatively best S/N, while those of $x = 6.806$ the relatively worst.

The "raw" effective scattering amplitudes in Fig.1 show directly the dimpling to depend on both, concentration and temperature. Doping does not significantly affect the overall behavior of the Y–O2,3–Ba (open circles), but moves that of Y–Cu2–Ba (closed circles, dashed line) for all temperatures clearly beyond Y–O2,3–Ba. Since the thermally induced damping is almost the same for both signals, the increasing difference may be straightforwardly attributed

to a relative linearization of Y–Cu2–Ba three body scattering geometry, *i.e.* the Cu2 atoms move off the O2,3 plane towards the Ba layer.

The temperature dependencies of the dimpling are displayed in Fig.2 in ascending order from the underdoped to the overdoped regimes. The numbers given at the left ordinates are from theoretical fits to the data using the high order MS approach of the FEFF6 code [8]. The data points, except for x=6.886, exhibit a surprisingly large scatter rendering unambigous determinations of the detailed temperature behaviours difficult. Therefore the superimposed lines ought to be understood as possible guides to the eyes, among others. Well known, many copper oxides are notoriously anomalous around $T \simeq 210$ K and $T \simeq 110$ K [7]. In fact, the dimpling exhibits cusps close to these temperatures, however, a systematic behaviour of these anomalies as a function of doping is hard to extract. Therefore we ignore them here. The dimpling of $x = 6.806$ and $x = 6.886$ may be seen to be independent on temperature within about ± 0.01 Å. However, the dimpling of underdoped $x = 6.886$ exhibits a shallow but clear minimum around 150 K; interestingly the step-like feature in Fig.1 at 110 K is almost cancelled. A minimum around 150 K may be also extracted from nearly optimum doped $x = 6.947$. In the overdoped regime the 150 K minimum vanishes: the dimpling of $x = 6.968$ is almost constant at $T \geq 100$ K, but increases at $T \leq 100$ K. Ignoring the strong cusp around 210 K the dimpling of overdoped $x = 6.984$ may be seen to increase linearily from 300 to 20 K.

4 Concluding Remarks

The dimples in the CuO_2 planes of doped $YBa_2Cu_3O_x$ and their variations with oxygen concentration and temperature appear to be intimately connected with its superconducting properties. The well known doping-induced increase of T_c is connected with increased dimples. A significant discontinuity occurs at the underdoped-overdoped phase separation line ($x = 6.95$). Some of us have recently shown that the discontinuity in the static dimpling correlates with a sudden drop of the Raman O2,3 in-phase shift (A_{1g} dimpling mode) at $x = 6.95$, giving hard evidence for a new displacive structural phase transformation in the CuO_2 planes [10]. The temperature dependent data presented in this report confirm the close connection between the dimpling and the transition from the underdoped into the overdoped regimes for $20 \leq T \leq 300$ K. Moreover, at least for underdoped $x = 6.886$, the dimpling appears to be unambigously connected to a characteristic temperature in the normal state, $T^* \simeq 150$ K.

Interestingly, the variations of the dimpling related with the dramatic variations of the superconducting properties on doping are comparatively weak,

$\simeq 0.05$ Å, *i.e* only $\simeq 20\%$ of the total dimpling. Thus its superconductivity related fraction may be seen to reside on top of an "offset" arising from the particular band structure [9].

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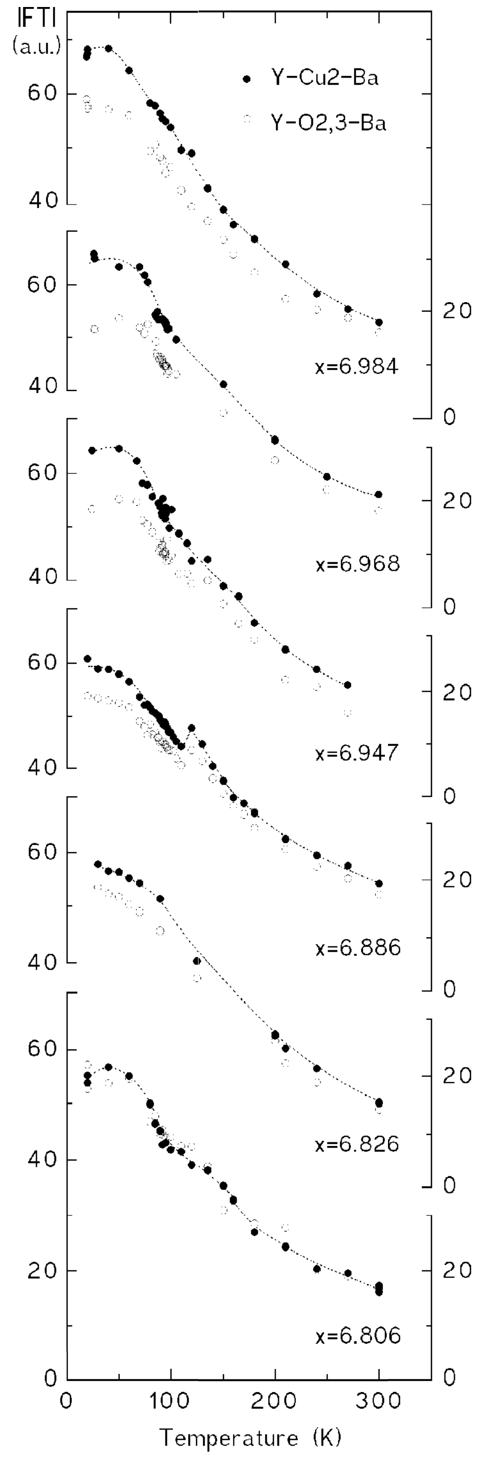
Figure captions

Fig.1: Effective scattering amplitudes (arbitrary units) of the Y–Cu2–Ba (closed circles) and the Y–O2,3–Ba (open circles) MS configurations in $YBa_2Cu_3O_x$ as a function of temperature and oxygen concentration, x. Dashed lines are guides to the eyes.

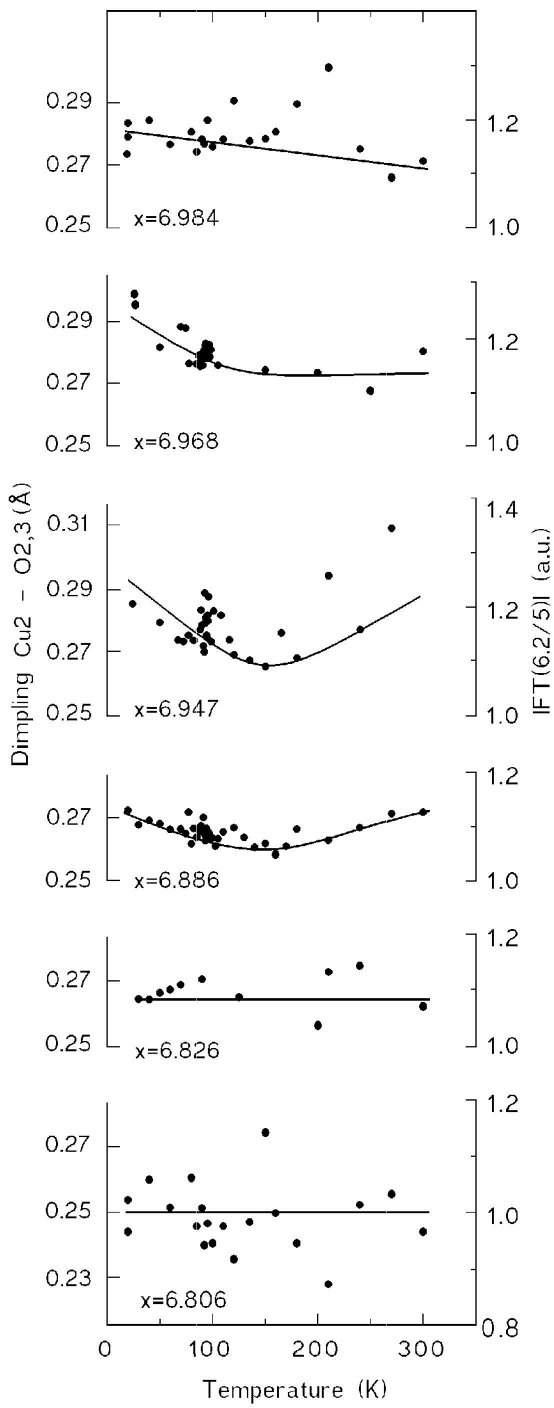
Fig.2: Dimpling of the CuO_2 planes in $YBa_2Cu_3O_x$ as a function of temperature and oxygen concentration, x. The superimposed lines are guides to the eyes. Right hand scale: ratio of the effective MS amplitudes displayed in Fig. 1.

□



|FT|
(a.u.)
Y-Cu2-Ba
Y-O2,3-Ba
x=6.984
x=6.968
x=6.947
x=6.886
x=6.826
x=6.806
Temperature (K)

Fig. 1



Dimpling Cu2 - O2,3 (Å)
IFT(6.2/5)I (a.u.)
x=6.984
x=6.968
x=6.947
x=6.886
x=6.826
x=6.806
Temperature (K)

Fig. 2